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### ARTICLE III.

*On the Extrication of the Alkalifiable Metals, Barium, Strontium, and Calcium.*  
*By Robert Hare, M. D., Professor of Chemistry in the University of Pennsylvania. Read October 4, 1839.*

IN the autumn of 1820, I devised an innovation in the mechanism and in the mode of completing the circuit of an *extensive* voltaic series. Previously to that time, in using any form of the voltaic battery, the circuit had always been completed by making a communication between the electrodes,\* after the submersion of the plates. In the case of the deflagrator, the electrodes might be made to communicate before the immersion of the plates, the circuit being completed by their immersion. Or, in case the electrodes should not be in contact before immersion, the operator was enabled to bring them together so nearly about the same time, as to avail himself of the pre-eminently energetic action which immediately succeeds the encounter between the plates and the solvent.

Fourteen years had elapsed, during which I had the regret of perceiving that the advantages of the deflagrator were not sufficiently estimated in Europe, when, about the year 1835, the celebrated Faraday,† while investigating the principles upon which galvanic apparatus should be constructed, came to a conclusion that the deflagrator eminently associated the requisites of which he

\* Agreeably to the suggestion of Faraday, I use the word electrode, for the pole of a voltaic series; also anode, for the positive pole, and cathode for the negative pole.

† See London and Edinburgh Philosophical Magazine and Journal, vol. viii., for 1836, p. 114.

was in search, and stated many facts and arguments tending to prove that it was the most perfect form of the apparatus at that time known. More than twelve years ago, while I was operating with a deflagrator of three hundred pairs, each seven inches by three, I observed that, in a circuit made through a saturated solution of chloride of calcium, by means of a coarse platina wire (No. 14) and a fine wire, (No. 26,) that when the latter was made the cathode and the former the anode, a most intense ignition resulted, causing the rapid fusion of the fine wire into globules like common shot. But when the situations of the wires were reversed, so that the smaller wire was made to form the anode, the ignition became comparatively so feeble as to be incompetent to fuse the fine platina wire. This phenomenon had continued to appear inexplicable, when, during the last winter, it occurred to me that the evolution and combustion of the calcium might be the cause of the superior heat produced at the cathode.

This led to the employment of chlorides in the process of Seebeck, Berzelius, and Pontin, for the production of amalgams from the earths, in which a cathode of mercury, and anode of platina were used. Accordingly, in operating with a deflagrator of three hundred and fifty Cruickshank pairs of seven inches by three, a mercurial amalgam was speedily obtained, which appeared sufficiently imbued with calcium to become speedily buried under a pulverulent stratum of lime, and mercury in a minute state of division.

Nevertheless, after exposure of the amalgam thus produced to the air, till all the calcium had been separated, and igniting the resulting powder to drive off the adhering mercury, the ratio of the weight of the lime thus obtained, to the mercury with which it had been united, was not over a five hundredth part. With a view to procure an amalgam in which the proportion of calcium should be greater, I was led to devise the following apparatus and process, of which an engraving and description is now laid before the society.

How far the result of my exertions, subsequently stated, may be considered in advance of the steps previously taken, will be evident from the fact that all the knowledge which exists, respecting the isolation of the metals of the alkaline earths, is due to the experiments and observations of Davy; and to what point they extended may be learned from the following quotations from the Bakerian lectures of that celebrated chemist. In reference to his efforts to isolate the radical in question, the distinguished lecturer mentions "that to obtain

a complete decomposition was extremely difficult, since nearly a red heat was required, and that at a red heat the bases of the earths acted upon the glass, and became oxygenated. When the tube was large in proportion to the quantity of amalgam, the vapour of naphtha furnished oxygen sufficient to destroy a part of the bases; and when a small tube was employed, it was difficult to heat the part used as a retort sufficiently to drive the whole of the mercury from the base without raising too highly the temperature of the part serving for a receiver so as to burst the tube." "When the quantity of amalgam was about fifty or sixty grains, I found that the tube could not be conveniently less than one-sixth of an inch in diameter, and of the capacity of about half a cubic inch. In consequence of these difficulties, in a multitude of trials I had few successful results; and in no case could I be absolutely certain that there was not a minute portion of mercury still in combination with the metals of the earths."\*

The observations are more than confirmed by my experience, which leads me to the conviction that the removal of the mercury is not to be accomplished thoroughly in glass vessels, and, of course, that Davy was perfectly correct in supposing that the products which he described as barium and strontium were alloys with mercury. I am also under the impression that the metals above mentioned decompose naphtha, when heated with its vapour, and enter into combination with its constituents. Had the barium which Davy obtained been free from mercury, it would not have been fusible below a red heat, as alleged by him. Agreeably to my experience, that metal requires no less than a good red heat for its fusion.

In a subsequent paragraph he adds: "The metal from lime I have never been able to examine exposed to air or under naphtha. In the case in which I was enabled to distil the mercury from it to the greatest extent, the tube unfortunately broke while warm, and at the same moment when the air entered the metal, which had the colour of silver, took fire and burnt, with an intense white light, into quicklime."\*

Had the failure of Sir Humphrey, in his efforts to isolate calcium, been due only to the accidental fracture of a glass tube, it would be inexplicable that a chemist so indefatigable should not have successfully reiterated the experi-

\* See Transactions of the Royal Society, part II. Nicholson's Journal, vol. xxi., for 1808; or, Tilloch's Philosophical Magazine, vol. xxxiii.

ment; or that no other chemist, during thirty intervening years, should have succeeded by resorting to the same means. No doubt exists in my mind that, without using a larger quantity of mercury than the sixty grains which he employed, and resorting to other materials than glass for a distillatory apparatus, no chemist could succeed in the isolation of calcium, nor in the complete distillation of the mercury from the amalgams of the other metals, so as to obtain available quantities for examination.

In a subsequent communication to the Royal Society, Davy mentions that, "by passing potassium through lime and magnesia, and then introducing mercury, I obtained solid amalgams, consisting of potassium, the metal of the earth employed, and mercury."

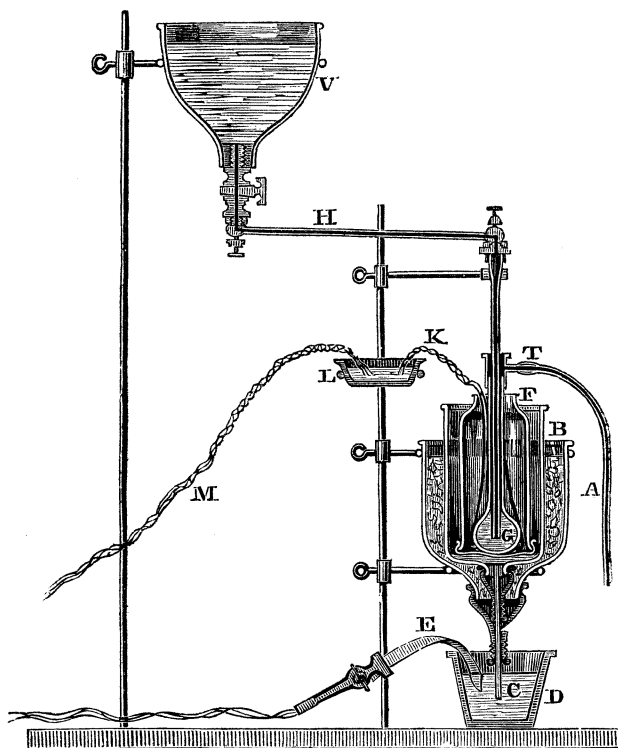
"The amalgam from magnesia was easily deprived of its potassium by water." Of the amalgam containing calcium he makes no farther mention, but suggests the possibility of obtaining, by operations performed in this manner, quantities of the metals of the earths sufficient for determining their nature and agencies.\*

But I will proceed to explain and describe the apparatus and process to which I have resorted, and to communicate the results which I have obtained.

*A Description of the Apparatus and Process for obtaining Amalgams of Calcium, Barium, and Strontium from saturated solutions of their Chlorides, by exposure to the Voltaic Circuit in contact with Mercury.*

A and B, two bell glasses, with perforated necks, were inverted and placed one within the other, so that, between them, there was an interstice of half an inch, which was filled with a freezing mixture. Concentrically within B a third similar bell, F, was placed, including a glass flask, of which the stem extended vertically through the neck of F. From a vessel, V, with a cock intervening, a tube luted to the orifice of the flask extended to the bottom of it, so as to convey thither from V a current of ice-water, which, after refrigerating the bulk of the flask, could escape through the nozzle projecting, horizontally, from the neck, T. The mercury in the capsule D communicates through the rod with the negative poles of one or more deflagrators. The capsule L in like manner with the corresponding positive poles.

\* 'Transactions Royal Society for 1810, part I., p. 62. Tilloch's Magazine, vol. xxxvi. p. 87.



A rod of platina reaches from some mercury in the capsule D, through the necks of the beds A and B, into a stratum of mercury, resting upon shoulder of the bell glass B, so as to be about a quarter of an inch beneath the flask. Several circumvolutions of platina wire, No. 14, forming a flat coil, were interposed between the mercury and the bottom of the flask. The recurved ends of this wire were made to reach into the mercury in the capsule L. Over the mouth of the bell F, after the introduction of the flask and coil, some bed-ticking was tied, so as to prevent contact between the platina and mercury, and to check, as much as possible, any reunion between the radical taken up by the one and the chlorine liberated by the other. Into the bell T, a saturated solution of the chloride to be decomposed was poured, and some coarsely powdered crystals of the same compound added. Of course the solution, by penetrating the ticking, came into contact with the mercury.

*Electrolytic Process.*

The peculiar mechanism of my apparatus, by which, in ten seconds, the acid may be thrown *on* or *off* of the plates, enables the operator, within that time, after a due arrangement of the poles is made, to put either or both of the deflagrators in operation, or to suspend the action of either or both. This mode of completing or breaking the circuit gives a great advantage in deflagrating wires; or in the processes, wherein dry cyanides, phosphurets, or carburets are to be exposed to voltaic action in vacuo, or in hydrogen. It enables us to arrange every part of the apparatus so as to produce the best effect upon the body to be acted upon, and then to cause a discharge of the highest intensity of which the series is capable, by subjecting the plates to the acid previously lying inactive in the adjoining trough.

In the case in point, where a chloride was to be decomposed, the deflagrators could be made to act through the same electrodes, either simultaneously or alternately. Of these facilities I thus availed myself:

Having supplied each deflagrator with a charge of diluted acid of one fourth of the usual strength, I began with No. 1, and at the end of five minutes superseded it by putting No. 2 into operation. Mean while, having added to No. 1 as much more acid as at first, at the end of the second five minutes I superseded No. 2 by No. 1; and, in like manner, again superseded No. 1 by No. 2. Having thus continued the alternate action of the deflagrators for about twenty minutes, both were made to act upon the electrodes simultaneously, the balance of acid requisite to complete the charge having been previously added.

By these means the reaction was rendered more equable than it could become in operating with one series more highly charged. Although, under such circumstances, the reaction may, at the outset, be sufficiently powerful to produce ignition, as I have often observed, after fifteen or twenty minutes it may become too feeble in electrolyzing power to render the continuance of the process in the slightest degree serviceable. Agreeably to my experience, as the ratio of the calcium to the mercury increases, the amalgam formed becomes so much more electro-positive as to balance the electro-negative influence of the voltaic current. After reacting with one series of two hundred pairs, of one hundred square inches each, for seventy minutes, I have found the proportion of calcium to be only one six-hundredth of the amalgamated mass obtained.

In this lies the great difficulty of obtaining any available quantity of the radicals of the alkaline earths by electrolyzation; especially in the case of calcium. It is easy, by a series of only fifty pairs, to produce an amalgam with that metal, which, when exposed to the air, will become covered with a pulverulent mixture of lime and mercury; but, in such case, the quantity of calcium taken up by the mercury, when estimated by the resulting oxide, will be found almost too small to be appreciated by weighing. To increase the quantity of calcium to an available extent I have found extremely difficult, since, as the process proceeds, the chemical affinity becomes more active while the electrolyzing power becomes more feeble.

That a change should be effected in mercury, giving to it the characteristics of an amalgam, by the addition of a six hundredth part of its weight, cannot be deemed difficult to believe, when it is recollected that Davy found that when, by amalgamation with ammonium, a globule of mercury had expanded to five times its previous bulk, it had gained, in weight, only one twelve thousandth part.\*

As the affinity between the chlorine and the radicals of the alkaline earths increases in strength with the temperature, and as heat is evolved in proportion to the energy of the voltaic action, the disposition of the elements separated by electrolyzation to reunite is, in this way, promoted. Hence the necessity of refrigeration.

The best index of the success of this process is the evolution of chlorine; since in proportion to the quantity of this principle extricated at the anode, must be the quantity of calcium separated at the cathode. During my operations, chlorine was evolved so copiously as to tinge the cavity of the innermost bell with its well known hue. Hence, when the evolution of chlorine ceases to be very perceptible, the amalgam should be extricated from the apparatus, and separated by a funnel and the finger from the solution of chloride, and immediately subjected to distillation.

It has been mentioned, that in the electrolytic process above described I resorted to the alternate action of two deflagrators. This was effected by making the negative poles of both communicate with the mercury in capsule D, while the positive poles communicated with some mercury in capsule L. For a description of the deflagrators employed, I refer to the American Philo-

\* See *Tilloch's Magazine*, vol. xxxiii. p. 213.



sophical Transactions, vol. v., or to Silliman's Journal, vol. xxxii. p. 285, as those which I employed were of the kind there described. There has, however, been an improvement introduced. Formerly, the plates were secured by cement; but, of late, I have had them so shaped and fitted as to slide out of the grooves when pulled by means of forceps. This has enabled me to have them washed after each operation, and, when necessary, scraped.

Instead of a coating of cement, the wood is defended by mutton suet or bees' wax, in which, while melted, it is soaked, after being made as hot as possible without taking fire.

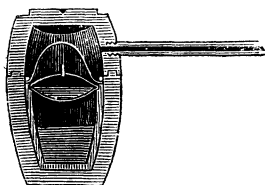
I have found great benefit to arise from Mr. Sturgeon's expedient of amalgamating the surfaces of the zinc; which Faraday has represented as giving, to a great extent, the properties of a sustaining battery. Agreeably to my experience, it renders the plates less liable to be encrusted with suboxide of zinc and copper, which always impairs the energy of a voltaic series.

In order to facilitate the insertion or extrication of the plates into or out of the grooves, the plates are cut so as to be about one-eighth in breadth less at the lower ends. In addition to the advantage of being enabled to cleanse the plates, this liberty of removing or replacing them is beneficial in another respect. It must necessarily ensue, that those edges of the plates which are lowermost, when the acid is in the act of being transferred, must be much more corroded than those portions of the surface which are otherwise situated. In fact, under the circumstances alluded to, the zinc is liable to be eaten through, near one of the lateral edges, when otherwise not more than half worn. But, in consequence of the construction above described, by a reversal of their relative position, each edge may, in turn, be made lowermost, so as to equalize the degree of corrosion sustained.

#### *Distillatory Apparatus and Process.*

A quantity of the amalgam, weighing about three thousand grains, was intro-

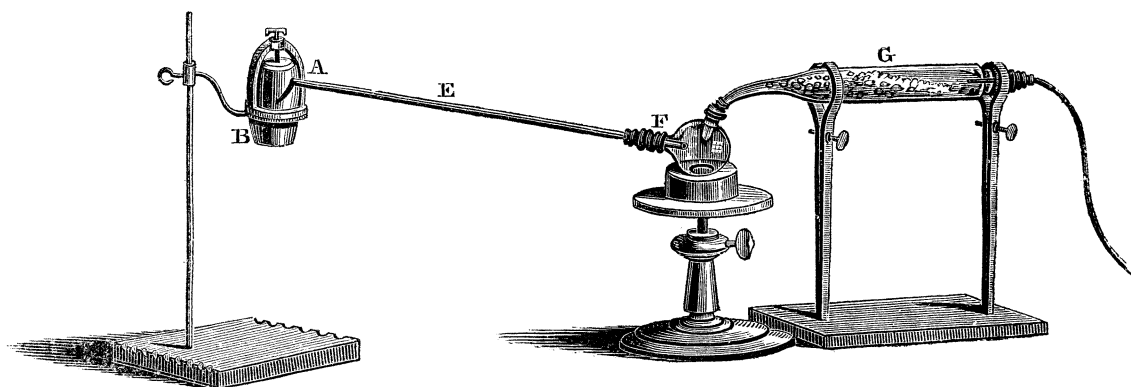
Fig. 2.



duced into an iron crucible. Of this crucible a section is represented by Fig. 2, which was forthwith closed by a capsule seated in a rabbet, or groove, made on purpose to receive it. The capsule being supplied with about half a dram of caoutchouchine, was then covered by the lid. In the next place, by means of a moveable handle, or bail,

of wire so constructed as to be easily attached, the crucible was transferred to the interior of the body of the alembic, A. Into the cavity thus occupied, about a dram measure of naphtha was poured. The canopy, A, and body of the alembic, B, were then joined, (as represented in Fig. 3,) with the aid of a luting of clay and borax between the grooved juncture and the pressure of the stirrup screw provided for that purpose.

Fig. 3.



A communication was made between the alembic and a small tubulated glass receiver, by means of an iron tube thirty inches long, and a quarter in bore. The tubulure of the receiver received the tapering end of an adopter, G, which communicated with a reservoir of hydrogen by means of a flexible lead pipe. The length of the tube prevented the alembic, or receiver, from being subjected to the agitation which results from the condensation of the mercurial vapour. Before closing the juncture completely, all the air of the alembic was expelled by a current of hydrogen, desiccated in its passage by a mingled mass of chloride of calcium and quicklime contained in the adopter. By keeping up the communication with the reservoir of this gas, while subjected to a column of about an inch or two of water, the pressure within the alembic being greater than without, there could be no access of atmospheric oxygen.

The bottom of the alembic was protected by a stout capsule of iron, (a cast iron mortar, for instance.) The next step was to surround it with ignited charcoal, in a chauffer or small furnace, taking care to cause the heat to be the greatest at the upper part. By these means, and the protection afforded by the mortar, the ebullition of the mercury may be restricted to the part of its mass nearest to the upper surface. Without this precaution, this metal is

liable to be thrown into a state of explosive vaporization, by which it is driven out of the crucible, carrying with it any other metal with which it may be united.

On the first application of the fire, the caoutchouchine distilled into the receiver. Next followed the naphtha from the body of the alembic. Lastly, the mercury of the amalgam distilled; the last portions requiring a bright red heat, in consequence of the affinity between the metal and the alkalisable radical.

After the distillation was finished, the apparatus having been well refrigerated, the alembic was opened and the crucible removed. As soon as the lid was taken off, some naphtha was poured between the rim of the capsule and sides of the crucible, so as to reach the metal below. This was found adhering to the bottom of the crucible.

When the heat was insufficient to carry off all the mercury, the metal was found in a state somewhat resembling metallic arsenic in texture, though its susceptibility of oxidation, and its affinity for carbon, caused it to be deficient of metallic lustre, until the surface was removed by the file or burnisher.

*Properties of the Metals obtained by the processes above mentioned.*

Either metal was rapidly oxydized in water, or in any liquid containing it; and afterwards, with tests, gave the appropriate proofs of its presence. They all sank in sulphuric acid; were all brittle and fixed; and, for fusion, required at least a good red heat. After being kept in naphtha, their effervescence with water is, on the first immersion, much less active. Under such circumstances they react, at first, more vivaciously with hydric ether than with water, or even chlorohydric acid; because in these liquids a resinous covering, derived from the naphtha, is not soluble, while to the ether it yields readily.

By means of solid carbonic acid, obtained by Mitchell's modification of Thilorier's process, I froze an ounce measure of the amalgam of calcium, hoping to effect a partial mechanical separation of the mercury by straining through leather, as in the case of other amalgams. The result, however, did not justify my hopes, as both metals were expelled through the pores of the leather simultaneously, the calcium forming, forthwith, a pulverulent oxide, intermingled with, and discoloured by mercury in a state of extreme division.

By the same means I froze a mass of the amalgam of ammonium as large as the palm of my hand, so as to be quite hard, tenacious and brittle. The mass floated upon the mercury of my mercurial pneumatic cistern, and gradually liquified, while its volatile ingredients escaped.

When the freezing of the amalgam was expedited by the addition of hydric ether, the resulting solid effervesced in water, evolving ethereal fumes. This seems to show that a portion of this ether may be incorporated with ammonium and mercury, without depriving the aggregate thus formed of the characteristics of a metallic alloy.